ON THE ULTRAVIOLET ABSORPTION SPECTRA OF ANISOLE IN THE LIQUID AND SOLID STATES*

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Plate IX

ABSTRACT. The absorption spectra of anisole ($C_6H_5.O.CH_3$) have been studied in the liquid and solid states in the ultraviolet region. In the liquid state three bands have been observed in the region 2650–2800 Å. Absorption again begins at about 2370 Å and total absorption occurs below 2330 Å. In the solid state at about −170°C, these three bands split up into six bands, with the first band at long wavelength side slightly shifted towards the shorter wavelength side from its position in the liquid state. It is pointed out that in the solid state at low temperatures the electronic energy levels are perturbed by the intermolecular field.

INTRODUCTION

It is well known that many organic substances in the vapour state exhibit bands with distinct structures in the ultraviolet absorption spectra and that in the liquid state the structure is modified owing to the influence of the intermolecular field. In the case of benzene, for instance, Kronenberger and Pringsheim (1926) observed that the absorption spectrum in the vapour state consists of a large number of bands, each consisting of a large number of narrower bands, and in the liquid state the absorption spectrum consists of only broad bands, the structure being hardly visible. In the solid state at −170°C again, the width of the individual bands diminishes considerably and fine structure is replaced by a few fainter absorption lines in the intervening regions.

The question whether the bands generally behave in the same way on lowering of temperature and on solidification in the case of aromatic organic compounds, having both polar and non-polar molecules, has not been fully investigated. Also it is only the comparison of the absorption spectra in the liquid and solid states that can show whether any profound change in the electronic energy levels of the molecules takes place with the change of state. Such an information would be helpful in understanding also the changes which take place in the Raman spectra of these substances with the change of state.

In a programme of work undertaken for this purpose, the absorption spectra of anisole in the liquid and solid states have been studied in the ultraviolet region in order to compare these with the absorption spectrum recorded by Sreeramamurty (1950) in the case of vapour, and to find out

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whether in the case of these polar molecules any striking change occurs with solidification of the liquid. The results have been discussed in the present paper.

EXPERIMENTAL

The source of ultraviolet continuum was a hydrogen discharge tube, made of pyrex glass, provided with quartz window and aluminium electrodes prepared in the laboratory. The tube was run at about 3 K.V. Pure anisole supplied by B.D.H-, was redistilled in vacuum three times before use. The liquid cell consisted of a pair of plane parallel quartz plates with a thin film of the liquid between them and held in a suitable brass frame. It was found that even the small thickness of the film was too large and produced total absorption in the region of the bands. The plates were then pressed together and very carefully slided along each other so as to reduce the thickness of the film. In this way it was possible to obtain a particular small thickness of the film which produced bands in the absorption spectrum.

For studying the absorption spectrum of the substance in the solid state, a Dewar vessel of fused silica was used to contain liquid oxygen, and the brass frame containing the cell with the liquid was introduced into the Dewar vessel, so that the lower part of the frame was dipped in liquid oxygen. No ice was found to be deposited on the surfaces of the cell, as the moisture

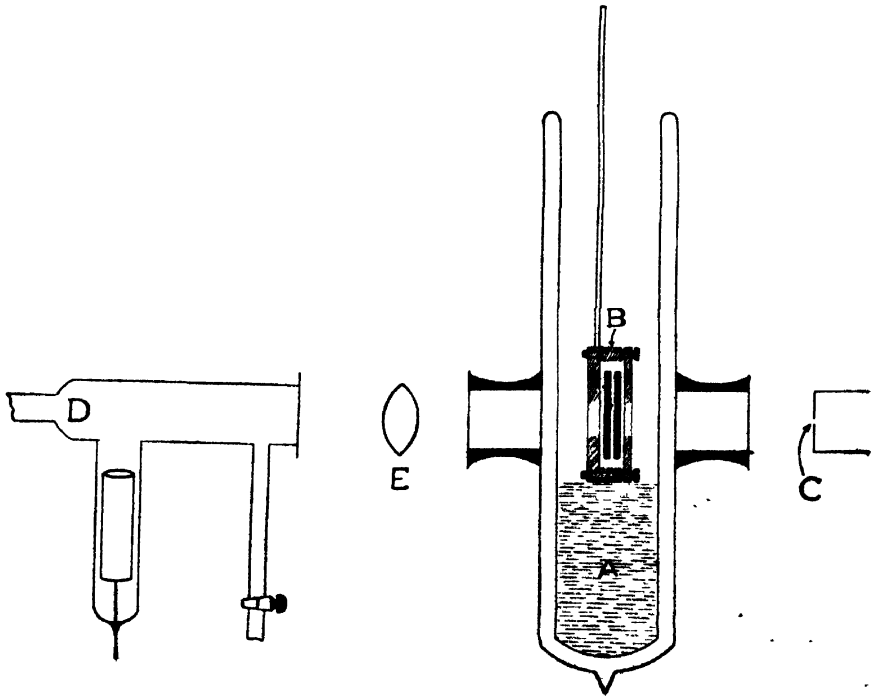
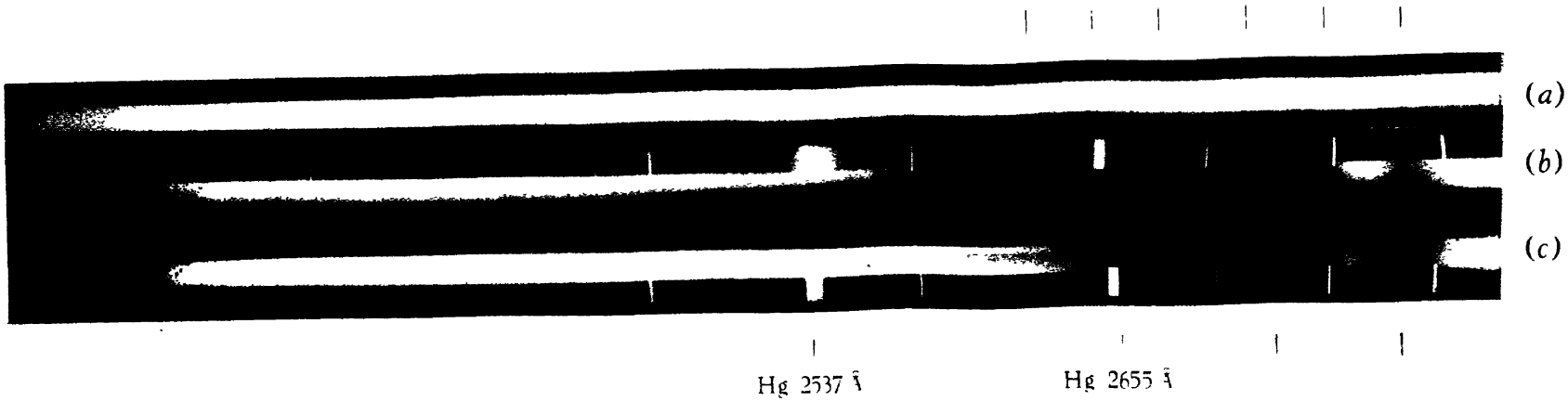


FIG. 1

A—Liquid oxygen
B—Brass frame containing the cell.
C—Spectrograph slit
D—Discharge tube
E—Quartz lens.



Absorption spectra of anisole.

(*a*) Hydrogen continuum
(*b*) Anisole—solid at about −170°C
(*c*) .. liquid .. .. 30°C

in the air was condensed at the mouth of the vessel. Entrance of moisture into the vessel was also prevented by the upward drift of air due to rapid evaporation of the liquid air. Two pieces of pyrex glass tube, each about one inch in length, were sealed on the opposite sides of the Dewar vessel with sealing wax and the ends closed by quartz plates in order to prevent deposit of moisture in the path of the light beam (Fig. 1.). To maintain a fairly steady temperature inside the cell, the level of the liquid oxygen was always kept just below the cell after allowing the lower portion of the brass frame to dip in the liquid oxygen.

An Adam Hilger E1 quartz spectrograph, giving a dispersion of about 3 A.U. per mm. in the region of 2600 Å was used in the present investigation. In the case of the liquid, an exposure of 6 minutes on Ilford H.P.3 films was sufficient, whereas, in the case of the solid an exposure of one and a half hours was necessary. This was due to the fact that the uneven walls of the Dewar vessel used in the latter case scattered away a large portion of the radiation.

RESULTS AND DISCUSSION

The absorption spectra for the substance in the liquid state at 30°C and in the solid state at about −170°C are reproduced in Plate IX. The wave numbers of the bands are given in Table I, along with those reported for the solution of anisole in ether by Kato and Someno (1938).

The sharp bands, large in number observed in the case of vapour (Sreeramamurty, 1950), are replaced by three broad bands in the liquid state. The spectrogram resembles that observed in the case of solution of anisole

TABLE I

	Soln. in ether (Kato & Someno)		Pure liquid at 30°C (Present author)				Solid at −170°C (Present author)			
Band	Wave no. cm^{-1}	Diff.	Band	Wave no. cm^{-1}	Diff.	Assignment	Band	Wave no. cm^{-1}	Diff.	Assignment
1	35900		1 (s)	35845		0−0	1 (s)	35870		0−0
		900			915				470	
2	36800		2 (vs)	36760		0+915	2 (s)	36340		0+470
		900			908				467	
3	37700		3 (w)	37668		0+2×911	3 (vs)	36807		0+2×468
		900							468	0+937
4	38600		4	...			4 (vs)	37275	421	0+3×468
							5 (w)	37696	460	0+2×913
										0+4×456
							6 (w)	38156		0+5×457

(s) — strong, (vs) — very strong, (w) — weak)

in ether by Kato and Someno (1938). They observed four bands, the frequency-difference between successive bands being 900 cm^{-1}, whereas, in the present investigation only three bands are observed. The centres of these broad bands at 35845, 36760 and 37668 cm^{-1} respectively, may correspond to the first three bands observed in the case of the solution. In the vapour state the o-o band observed by Sreeramamurty (1950) is at 36359 cm^{-1}. This shows that the bands have shifted towards the longer wavelength side with change from vapour to liquid phase. When the liquid is solidified, three bands, corresponding to those observed in the case of the liquid, are observed in positions slightly shifted towards shorter wavelengths and each of these three bands is further followed by another band shifted from the former by about 460 cm^{-1} towards shorter wavelengths.

This phenemenon cannot be considered as sharpening and splitting up of the broad bands in the solid state, because in the position of the three new bands there are no absorption minima in the case of the liquid. Also the new frequency-shift 460 cm^{-1} between the first and the second band observed in the case of the solid is not observed in the case of the liquid. From these facts it can be concluded that the electronic configuration in the molecule undergoes changes with solidification of the substance. From a comparision of the absorption spectrum of the vapour reproduced by Sreeramamurty (1950) with that for the liquid observed in the present investigation, it is found that the structure of the bands observed by the former author is absent in the case of the liquid. This again is due to the influence of the intermolecular field in the liquid state. It has to be pointed out in this connection that the bands on the longer wavelength side of o-o band observed by Sreeramamurty are not observed in the case of the liquid in the present investigation. Further, theoretically the intensity of the o-1301 or o-1412 band ought to be too feeble to be recorded in the spectrogram.

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